

BRIGHT STUFF ON CERES = SULFATES AND CARBONATES ON CI CHONDRITES. Michael Zolensky¹, Queenie H.S. Chan¹, Matthieu Gounelle^{2,3}, Marc Fries¹. ¹ARES, NASA Johnson Space Center, Houston TX 77058 USA (Michael.e.zolensky@nasa.gov); ²Muséum National d'Histoire Naturelle, 75005 Paris, France; ³Institut Universitaire de France, 75005 Paris, France.

Introduction: Recent reports of the DAWN spacecraft's observations of the surface of Ceres indicate that there are bright areas, which can be explained by large amounts of the Mg sulfate hexahydrate ($\text{MgSO}_4 \cdot 6(\text{H}_2\text{O})$) [1], although the identification appears tenuous. There are preliminary indications that water is being evolved from these bright areas, and some have inferred that these might be sites of contemporary hydro-volcanism. A heat source for such modern activity is not obvious, given the small size of Ceres, lack of any tidal forces from nearby giant planets, probable age and presumed bulk composition. We contend that observations of chondritic materials in the lab shed light on the nature of the bright spots on Ceres.

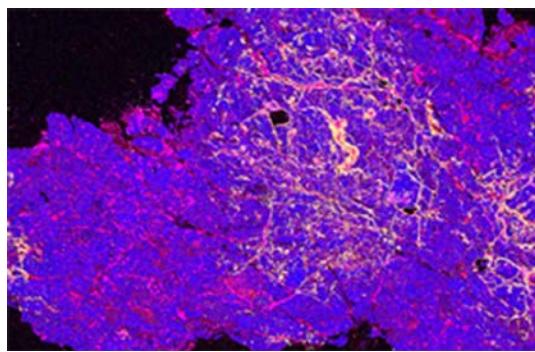


Figure 1. Element map of an Orgueil thin section, with evident, modern sulfate veining. Mg-Blue, Na-Yellow, S-Red. View measures 5 mm across. Note Na-Mg zoning in the wider veins. Note that the majority of the Na-rich veins are in one region.

Sulfate veins have been reported in CI chondrites for over a century [2,3], but Gounelle and Zolensky [4] have convincingly shown that the bulk or perhaps entirety of these veins are of terrestrial origin. That is, they formed after the meteorites were recovered on Earth. Anyone who has obtained CI chondrite samples, tucked them away for a period of several years or more, and then examined them will have noticed the appearance of white surface sulfate efflorescence. We have observed the same phenomenon on CI chondrite polished and thin sections, potted butts retained after partial microtomy of CI grains, and even partially microtomed chondritic IDPs, especially when stored in a dry place. These modern sulfates must have formed by dissolution of

very unstable, pre-terrestrial phases (sulfates, chlorides, sulfites, ammoniacal salts, etc.), followed by re-precipitation at the dry surface. We do not know what the hygroscopic pre-terrestrial phases were, but oldhamite (CaS) is one possibility. Long thought to be present only in enstatite chondrites, this phase was recently found in the Sutter's Mill C2 chondrite recovered immediately after its fall [5]. What other unstable phases have we missed seeing in chondrites?

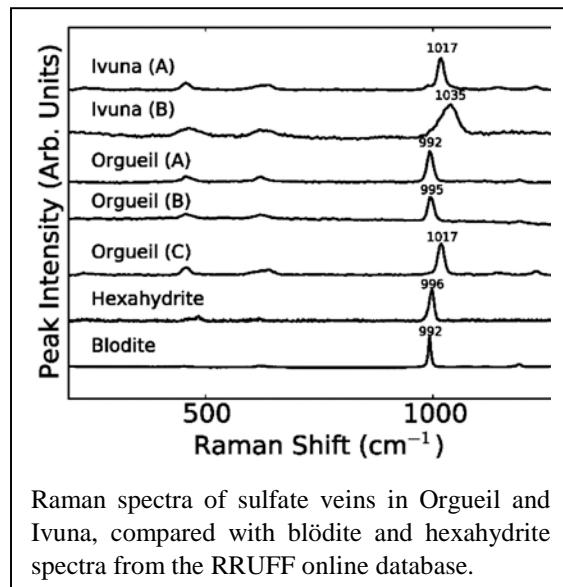
We have been reexamining sections of Orgueil and Ivuna that we made approximately 15 years ago. Since our goal at that time was a search for aqueous fluid inclusions, we made thin and polished sections of the meteorites without use of any water or cutting or polishing oil. We used only samples that had never been in contact with water since recovery (i.e. none had been sliced or prepared previously). The prepared samples have been maintained in sealed cabinets flooded with dry, curation-grade nitrogen except for brief periods when samples have been exchanged. We were therefore surprised to see considerable eruptions of white minerals on the surfaces of all prepared sample, with the amount of white material being inhomogeneous in quantity and composition.

Analytical methods: We examined the new-formed, white phases using Raman spectroscopy to definitively determine the mineralogy. Raman spectra were collected at JSC using a Jobin-Yvon LabRAM HR800. The spectrometer was equipped with an argon ion (Ar+) gas laser, the excitation source was at a wavelength of 514.53 nm, and the laser power was ~450 µW at the sample surface to minimize beam damage. The laser light was focused to a spot size of ~1 µm on the surface. Three accumulated spectra were collected from each spot to identify and discard spurious signals, such as those from cosmic rays.

We then examined the same samples using a FEGSEM, to document phase morphologies and textures. We used a JEOL 7600F field emission SEM equipped with windowless, thin window, and Be window EDS detectors, and a Link backscattered electron detector, all at JSC.

Results: Raman spectrometry revealed that the bulk of the encrustations on Orgueil are blödite ($\text{Na}_2\text{Mg}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$) and a Mg-sulfate whose identity we are still considering (library Raman spectra for Mg sulfates are not extensive). Ni-Blödite was

tentatively identified in CI chondrites by Fredriksson and Kerridge [2], based solely on chemistry, although they assumed that this was pre-terrestrial in origin. We observed only trace Ni in sulfates. Grains rich in organic materials are also locally abundant in the sulfate veins, indicating that these were entrained within the percolating fluids that moved through the samples. This in turn suggests that the original, pre-terrestrial phase that dissolved, to later re-precipitate as surface veins, contained abundant organic grains. We similarly found broken pieces of Ca carbonates, which must also have been carried to the sample surfaces by the percolating fluids.



Raman spectra of sulfate veins in Orgueil and Ivuna, compared with blödite and hexahydrite spectra from the RRUFF online database.

The element map of the Orgueil section reveals that some Orgueil lithologies are covered with blödite, whereas others are not. Mg-sulfates were everywhere. This suggests that the composition of the newly grown sulfate veins is controlled by the bulk composition of the lithology, and, obviously, the extent of available easily dissolved Na-, Mg-bearing phases. For Ivuna, we examined chips, not prepared thin sections. Here again, samples were broken about 15 years ago, at which time no significant amounts of white surface phases were evident. Now it is a very different story – they are abundant. We have recently observed the same situation for the large mass of Ivuna preserved at the Natural History Museum, London.

Based on our SEM-EDX analyses, freshly-formed Mg and Mg-Ca sulfates dominate the surface efflorescences on Ivuna. Mixed in among these are organic grains (Figure 3), and broken pieces of Ca carbonates, probably also entrained by the fluids percolating through the sample.

The organic grains were characterized by D and G bands in Raman spectra (Figure 3); in Orgueil organics were burned by the Raman beam, precluding analysis.

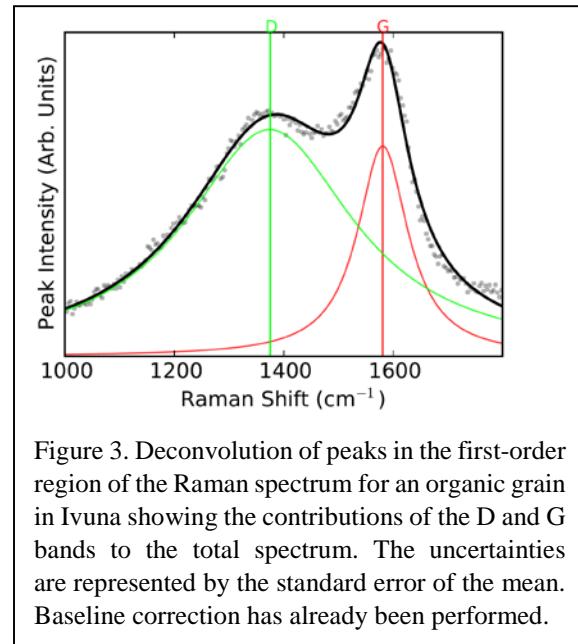


Figure 3. Deconvolution of peaks in the first-order region of the Raman spectrum for an organic grain in Ivuna showing the contributions of the D and G bands to the total spectrum. The uncertainties are represented by the standard error of the mean. Baseline correction has already been performed.

Discussion: Despite the fact that our CI samples were carefully maintained in a dry, non-oxidizing atmosphere, abundant sulfates have precipitated at sample surfaces. Obviously, a small amount of water (possibly including pre-terrestrial water) has dissolved hydroscopic phases within the samples, and they were drawn to the surface where water evaporated and sulfates were precipitated. We propose that a similar process has formed the white deposits on the surface of Ceres, and that modern hydro-volcanism was not necessary. We predict that abundant carbonates and organics will also be found in the Ceres bright areas. Finally, surface efflorescences of sulfates on C asteroids should provide a mechanism for Na and S loss from asteroids, as micrometeorite impacts preferentially sputter away these species from friable sulfates.

Acknowledgements: We thank Eve Berger for assistance with the SEM, Ed Cloutis for many standards and useful discussion, and Loan Le for help with the Raman analyses. MZ was supported by the NASA Cosmochemistry Program, and David Kring's SERVII grant.

References: [1] Nathues et al. (2015) *Nature* **528**, 237–240; [2] Fredriksson and Kerridge (1988) *Meteoritics* **23**, 35–44; [3] Airieau et al. (2005) *GCA* **69**, 4166–4171; [4] Gounelle and Zolensky (2001) *MAPS* **36**, 1321–1329; [5] Zolensky et al. (2014) *MAPS* **49**, 1997–2016.